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TYPES OF ADSORBENT AND RELATIONSHIPS BETWEEN R_M VALUES OF A SUBSTANCE AND THE COMPOSITION OF THE MOBILE PHASE IN THIN-LAYER CHROMATOGRAPHY

JAN K. RÓŻYŁO

Department of Physical Chemistry, Institute of Chemistry, M. Curie-Skłodowska University, Nowotki 12, Lublin 20-031 (Poland)

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SUMMARY

Relationships between R_M values of substances and the adsorption data for the components of the mobile phase and its composition were investigated, using silica gel G and aluminium oxide G as adsorbents. The substances chromatographed were quinoline derivatives, fluorenone and carbazole. The mobile phases were benzene-chloroform and benzene-acetone mixtures.

The results showed good agreement between the theoretical and experimental relationships $R_{M1,2} = f(\varphi_1)$ (where φ_1 is the composition of the mobile phase) on the two adsorbents. The results indicate that it may be possible to extend the interpretation of the chromatographic process and to predict the optimal conditions for the separation of mixtures on different types of adsorbents to a greater extent than has been permitted so far.

INTRODUCTION

The wide application of thin-layer chromatography (TLC) in the direct control of chemical processes in industry and in the laboratory necessitates investigations that would permit the rapid and accurate prediction of the optimal separation conditions and the correct interpretation of the chromatographic process. So far, the most interesting theoretical investigations in this field have been those by Snyder¹⁻³, Turina *et al.*⁴, Soczewiński and co-workers⁵⁻⁷ and Ościk and co-workers⁸⁻¹¹.

The theory deduced by Ościk and co-workers, based on the thermodynamics of the process of adsorption from solution, permits a relationship to be derived between certain thermodynamic values and chromatographic parameters. For this reason, this theory was chosen as the starting point in the present investigations.

The equation that results from this theory, which has been discussed earlier¹⁰⁻¹⁶, permits the R_M values of the chromatographed substances to be related simply to the adsorption data of the components of the liquid mobile phase and to the composition of the phase:

$$R_{M1,2} = \varphi_1 \Delta R_{M1,2} + (\varphi_1^2 - \varphi_1)(\Delta R_{M1,2} + A_2) + R_{M2} + Y \quad (1)$$

where R_M is related to the R_F value by the equation

$$R_M = \log \left(\frac{1 - R_F}{R_F} \right) \quad (2)$$

$R_{M_{1,2}}$ represents the R_M value of a substance z obtained by using a two-component solvent mixture consisting of solvents 1 and 2; R_{M_1} and R_{M_2} represents the R_M values of the substance z obtained when using pure solvents 1 and 2, respectively, as the mobile phase, so that

$$\Delta R_{M_{1,2}} = R_{M_1} - R_{M_2} \quad (3)$$

φ_1 represents the volume fraction of solvent 1 in the two-component solvent mixture in the mobile phase and φ_1^s represents the volume fraction of solvent 1 of the two-component solvent mixture in the surface phase. Hence the difference $\varphi_1^s - \varphi_1$ expresses the adsorption of the components of the binary mobile phase, and can be determined experimentally from the adsorption isotherms of the mobile phase components. By defining the distribution function of the components of the mobile phase as

$$K_1 = \frac{\varphi_1^s (1 - \varphi_1)}{\varphi_1 (1 - \varphi_1^s)} \quad (4)$$

we obtain

$$\varphi_1^s - \varphi_1 = \frac{\varphi_1 (K_1 - 1)(1 - \varphi_1)}{1 + (K_1 - 1)\varphi_1} \quad (5)$$

When using ideal or conformal (regular) mixtures as the mobile phase, it can be assumed that

$$-\log K_1 = \Delta R_{M_{1,2}} \quad (6)$$

It is then possible to estimate the distribution function, K_1 , from the chromatographic data of the substance using pure solvents as the mobile phase. Thus, from eqn. 5 it is possible to calculate the difference $\varphi_1^s - \varphi_1$ for each component of the mobile phase, without using adsorption isotherm data.

Δz in eqn. 1 represents $\log k_{1,2}^\infty$, where $k_{1,2}^\infty$ is the hypothetical partition coefficient of substance z between components 1 and 2 of the binary solvent mixture. This coefficient represents the interaction between the molecules of substance z and those of the components of the solvent mixture (mobile phase).

Y is a value that depends on the type of substance being chromatographed and on the mobile phase components. For ideal mobile phases it is zero. For mobile phases that represent conformal (regular) solutions, Y is small for each mobile phase composition and can be disregarded.

A detailed discussion and the means of using the above equations were given in earlier papers¹⁰⁻¹⁵. The agreement between theoretical values estimated by means of this equation and experimental values was demonstrated for systems of mixed ideal

or conformational solvents used as mobile phases. All measurements were carried out on silica gel as adsorbent.

Generalization of the above theoretical considerations will be possible after extending the investigation to adsorbents that differ considerably in their properties. Of course, when using liquid mobile phases that are not ideal solutions, values such as the distribution function K_1 and the partition coefficient $k_{1,2}^\infty$ in a given case cannot possibly have the same physical meaning as that for ideal systems. Earlier considerations^{14,15} permit the assumption that quantitative analysis of the parameters in eqn. I will also allow the analysis of a chromatographic process by using solvents that have properties different from those of ideal solutions.

The mechanism of adsorption in chromatography on aluminium oxide differed from that observed on silica gel. Aluminium oxide is the most widely used adsorbent, apart from silica gel, for the chromatographic analysis of petroleum products¹⁷. As a result of structural differences between aluminium oxide and silica gel¹⁸, alcohols, for example, may be weaker eluents on silica gel than on aluminium oxide in comparison with other solvents.

The above considerations prompted investigations aimed at comparing the theoretical and experimental relationships between the R_{Mz} values of a substance and the composition of the mobile phase on two different adsorbents, *viz.*, aluminium oxide and silica gel.

EXPERIMENTAL

Experimental functions $R_{M1,2} = f(\varphi_2)$ were obtained by measuring the R_F values of substances (Table I) by ascending TLC. Silica gel G and aluminium oxide G for TLC (activity I) (Merck, Darmstadt, G.F.R.) were used as adsorbents. The model substances chromatographed were quinoline, isoquinoline, 2-methylquinoline, 4-methylquinoline and fluorenone (class B) and carbazole (class AB) according to the classification of Pimentel and McCiellan¹⁹, each having electron-donor properties. Benzene-chloroform (N + A) and benzene-acetone (N + B) mixtures were used as mobile phases. The solvent systems are relatively simple, especially when the polar component is non-associated. The influence of the composition of the mobile phase on the adsorption of the chromatographed substance will depend to some extent on the solvation constant in this phase, and the actual situation in such a chromatographic system may be different from that in a known model system when theoretical parameters are predicted. The above liquid mobile phase systems are those most often used in adsorption chromatography, which is why they were chosen for these experiments.

Chromatography was carried out in the usual way, as described in detail elsewhere^{12,13,15,20,21}. The results are presented as graphs of $R_{M1,2} = f(\varphi_1)$ obtained theoretically on the basis of the eqn. I (solid and broken lines) and experimentally (points).

The values of the distribution function K_1 , characteristic of the adsorption of the components of the liquid mobile phase, were found by assuming that $-\log K_1 = \Delta R_{M1,2}$. This value permitted, in turn, the difference $\varphi_1^z - \varphi_1$ to be found¹²⁻¹⁵. Suitable values of $A_z = \log k_{1,2}^\infty$ were chosen for the calculated function $R_{M1,2} = f(\varphi_1)$ (ref. 10). The values of A_z give an idea of the molecular interactions between the molecules of substance z and those of the components of the solvents.

TABLE I

 R_F VALUES OF SOLUTES CHROMATOGRAPHED ON ALUMINIUM OXIDE AND SILICA GEL

Mobile phases: benzene-chloroform and benzene-acetone.

Solute	$C_6H_6-CHCl_3$			$C_6H_6-(CH_3)_2CO$		
	Vol. fraction of $CHCl_3$	R_F		Vol. fraction of $(CH_3)_2CO$	R_F	
		Al_2O_3	SiO_2		Al_2O_3	SiO_2
Quinoline	0.0	0.30	0.03	0.0	0.30	0.03
	0.1	0.34	0.04	0.1	0.69	0.19
	0.3	0.38	0.06	0.3	0.87	0.58
	0.5	0.40	0.07	0.5	0.91	0.69
	0.7	0.50	0.07	0.7	0.91	0.75
	0.9	0.52	0.07	0.9	0.91	0.75
	1.0	0.56	0.07	1.0	0.91	0.70
Isoquinoline	0.0	0.14	0.01	0.0	0.14	0.01
	0.1	0.20	0.04	0.1	0.14	0.01
	0.3	0.28	0.07	0.3	0.74	0.52
	0.5	0.33	0.08	0.5	0.79	0.65
	0.7	0.32	0.09	0.7	0.80	0.71
	0.9	0.43	0.08	0.9	0.78	0.71
	1.0	0.37	0.08	1.0	0.74	0.67
2-Methylquinoline	0.0	0.32	0.02	0.0	0.32	0.02
	0.1	0.42	0.04	0.1	0.69	0.22
	0.3	0.46	0.07	0.3	0.87	0.62
	0.5	0.53	0.07	0.5	0.89	0.76
	0.7	0.56	0.08	0.7	0.90	0.84
	0.9	0.57	0.09	0.9	0.86	0.81
	1.0	0.61	0.09	1.0	0.79	0.76
4-Methylquinoline	0.0	0.16	0.02	0.0	0.16	0.02
	0.1	0.28	0.04	0.1	0.63	0.17
	0.3	0.35	0.04	0.3	0.83	0.50
	0.5	0.40	0.07	0.5	0.88	0.59
	0.7	0.42	0.05	0.7	0.85	0.68
	0.9	0.38	0.05	0.9	0.84	0.69
	1.0	0.50	0.05	1.0	0.79	0.68
Fluorenone	0.0	0.59	0.28	0.0	0.59	0.28
	0.1	0.73	0.38	0.1	0.66	0.43
	0.3	0.81	0.48	0.3	0.78	0.65
	0.5	0.75	0.54	0.5	0.85	0.77
	0.7	0.75	0.57	0.7	0.90	0.88
	0.9	0.80	0.59	0.9	0.93	0.91
	1.0	0.91	0.59	1.0	0.93	0.93
Carbazole	0.0	0.60	0.48	0.0	0.60	0.48
	0.1	0.70	0.51	0.1	0.66	0.65
	0.3	0.77	0.59	0.3	0.77	0.82
	0.5	0.78	0.62	0.5	0.84	0.88
	0.7	0.79	0.62	0.7	0.85	0.93
	0.9	0.77	0.68	0.9	0.88	0.94
	1.0	0.76	0.68	1.0	0.87	0.95

TABLE II

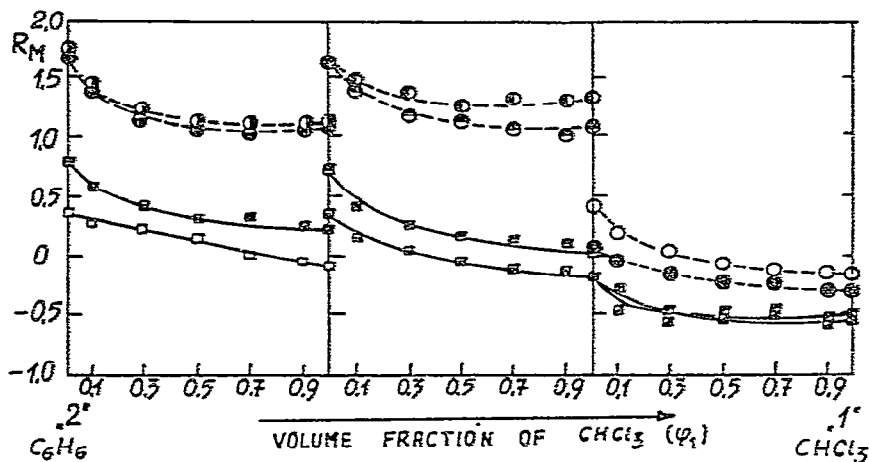
VALUES OF A_2 AND K_1 OF SOLUTES CHROMATOGRAPHED ON ALUMINIUM OXIDE AND SILICA GEL AS ADSORBENTS

Mobile phases: benzene-chloroform and benzene-acetone.

Solute	$C_6H_6-CHCl_3$				$C_6H_6-(CH_3)_2CO$			
	A_2		K_1		A_2		K_1	
	Al_2O_3	SiO_2	Al_2O_3	SiO_2	Al_2O_3	SiO_2	Al_2O_3	SiO_2
Quinoline	+0.62	-0.43	+3.3	+3.5	-0.23	0.0	+16.0	+81.22
Isoquinoline	-0.21	-0.56			-0.50	+0.51		
2-Methylquinoline	-0.06	-0.92			-0.25	-0.04		
4-Methylquinoline	-0.26	-0.54			-0.67	+0.29		
Fluorenone	-1.32	-0.16			0.0	+1.23		
Carbazole	-1.88	+0.18			-0.69	+0.87		

RESULTS AND DISCUSSION

The experimental results show two cases, when the mixed mobile phase consists of an active solvent of either A or B type plus an N-type solvent. In N + B systems, solvation effects may also be observed, while the interaction of acetone with the adsorbent surface (silica) may result in complexes with surface hydroxyl groups²².



Al_2O_3	□	■	▣	▤	▥	▦
SiO_2	○	⊙	⊖	⊕	⊗	⊘
SOLUTE	<chem>c1ccc2c(c1)ncn2</chem>	<chem>c1ccc2c(c1)ncn2</chem>	<chem>Cc1ccc2c(c1)ncn2</chem>	<chem>Cc1ccc2c(c1)ncn2</chem>	<chem>O=C1C=CC=C2C(=O)N1C2</chem>	<chem>C1=CC=C2C(=C1)N=C2</chem>

Fig. 1. Theoretical (solid and broken lines) and experimental (points) $R_{M,1,2} = f(\varphi_1)$ relationships for quinoline, isoquinoline, 2-methylquinoline, 4-methylquinoline, fluorenone and carbazole obtained on aluminium oxide (squares) and silica gel (circles). Mobile phase: benzene-chloroform.

In agreement with Snyder²³, for molecular complexes in the liquid phase between molecules of a solvent and molecules of a chromatographed substance, the energy of interaction will not be determined by the adsorption energy of the substance but by the adsorption energy of the complex formed.

Soczewiński and Matysik²⁴ reported that quinoline derivatives used as model substances do not form hydrogen bonds with ketone (acetone) molecules. However, this does not mean that in the systems examined interactions of another type might not occur.

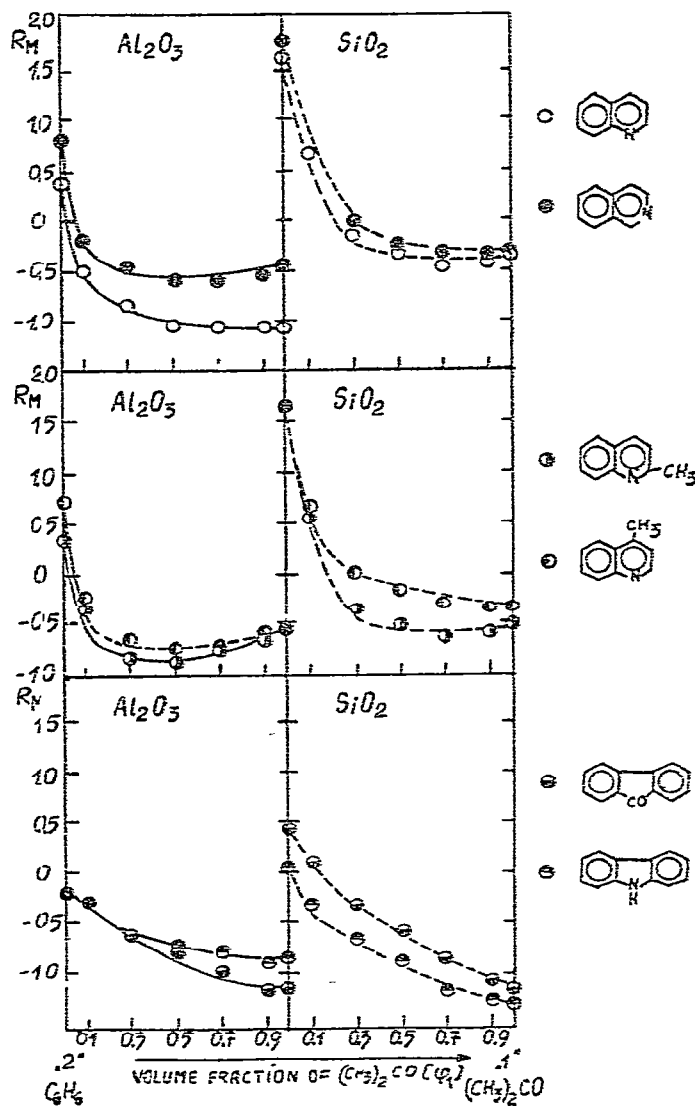


Fig. 2. Theoretical (solid and broken lines) and experimental (points) $R_{M,2} = f(\varphi_1)$ relationships for quinoline, isoquinoline, 2-methylquinoline, 4-methylquinoline, fluorenone and carbazole obtained on aluminium oxide and silica gel. Mobile phase: benzene-acetone.

In the methyl-substituted quinolines examined, mesomeric effects can also occur, although it seems that steric effects prevail with 2-methylquinoline. This is shown by the different values of A_z for this substance (Table II) in comparison with those for other quinoline derivatives. The negative values of A_z observed for the substances examined illustrate the stronger interactions of the substances with the less active component of the mobile phase. It is interesting that these values do not depend on the type of adsorbent.

For the benzene-chloroform mobile phase, the values of the adsorption equilibrium constant (distribution function) are very close on both adsorbents ($K_1 = 3.3-3.5$), while for the benzene-acetone mobile phase the values differ widely (16.0 on aluminium oxide and 81.22 on silica gel).

Fig. 1 shows the relationships $R_{M1,2} = f(\varphi_1)$ for the quinoline derivatives and fluorenone and carbazole obtained on the two adsorbents with benzene-chloroform as the mobile phase. There is a fairly good agreement between the experimental and theoretical relationships on both adsorbents. For the quinoline derivatives, both the theoretical and experimental relationships differ largely in the R_M values of the substances examined. However, the shapes of the curves are similar.

A comparison of the $R_{M1,2} = f(\varphi_1)$ relationships and the values of K_1 on the adsorbents used indicates a close similarity between the adsorption processes undergone by the molecules of the mobile phase in the two chromatographic systems. Similar shapes of the theoretical and experimental $R_{M1,2} = f(\varphi_1)$ functions were observed when using fluorenone and carbazole.

A different shape of the theoretical and experimental $R_{M1,2} = f(\varphi_1)$ relationships can be seen in Fig. 2, which shows that the functions differ on the two adsorbents with regard to both R_M values and shape. The benzene-acetone mobile phase shows the presence of more complex and stronger molecular interactions, the change in the molecular interactions being indicated by the very different $\Delta R_{M1,2}$ values for the substances.

The theoretical and experimental results indicate the possibility of extending the use of the equation to a larger number of adsorbents. It is hoped that eqn. 1 may be used for the prediction of optimal separation conditions of mixtures of substances and for the interpretation of the chromatographic process to a greater extent than that suggested by current investigations.

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